9.0 PHYSICAL ANALYSIS OF SEDIMENT AND CHEMICAL ANALYSIS OF SEDIMENT, WATER, AND TISSUE SAMPLES

This section provides guidance on the selection of chemical and physical analyses to aid in the evaluation of dredged material for proposed disposal, and on the methods used to analyze these parameters. QA/QC guidance is provided in Appendix G and EPA (1995).

The methods cited in this section may be used to develop the required chemical information. However, other methods may provide similar results, and the final choice of analytical procedures depends upon the needs of each evaluation. In all cases, proven, state-of-the-art methods should be used.

Any dredged material from estuarine or marine areas contains salt. The salt can interfere with the results obtained from some analytical methods. *Any methods proposed for the analysis of sediment and water from estuarine or marine environments must explicitly address steps taken to control salt interference.*

9.1 Physical Analysis of Sediment

Physical characteristics of the dredged material must be determined to help assess the impact of disposal on the benthic environment and the water column at the disposal site. This is the first step in the overall process of sediment characterization, and also helps to identify appropriate control and reference sediments for biological tests. In addition, physical analyses can be helpful in evaluating the results of analyses and tests conducted later in the characterization process.

The general analyses may include (1) grain size, (2) total solids and (3) specific gravity.

Grain-size analysis defines the frequency distribution of the size ranges of the particles that make up the project sediment (e.g., Plumb, 1981; Folk, 1980). The general size classes of gravel, sand, silt, and clay are the most useful in describing the size distribution of particles in dredged-material samples. Use of the Unified Soil Classification System (USCS) for physical characterization is recommended for the purpose of consistency with USACE engineering evaluations (ASTM, 1992).

Total solids is a gravimetric determination of the organic and inorganic material remaining in a sample after it has been dried at a specified temperature. The total solids values generally are used to convert concentrations of contaminants from a wet weight to a dry weight basis.

The specific gravity of a sample is the ratio of the mass of a given volume of material to an equal volume of distilled water at the same temperature (Plumb, 1981). The specific gravity of a dredged-material sample helps to predict the behavior (i.e., dispersal and settling characteristics) of dredged material after disposal.

Other physical/engineering properties (e.g., Atterburg limits, hydrometer analysis, settling properties, etc.) may be needed to evaluate the quality of any effluent discharged from confined disposal facilities. Guidance in this regard is provided in Appendix B.

9.2 Target Detection Limits

The selection of appropriate target detection limits (TDLs) is vital (e.g., TetraTech, 1986a; EPA, 1986a). TDLs should be lower than the appropriate values against which the data are to be compared for interpretation. Different analytical methods are capable of detecting different concentrations of a chemical in a sample. For example, a highly sensitive technique can detect a much lower chemical concentration than can a screening technique for the same chemical. The accuracy of measurements also differs among analytical techniques. In general, as the sensitivity and accuracy of a technique increases, so does the cost. Recommended TDLs that are judged to be feasible, cost effective, and to meet the requirements for dredged material evaluations are summarized in EPA (1995), along with example analytical methods that are capable of meeting those TDLs. However, any method that can achieve those TDLs is acceptable, provided that the appropriate documentation of the method performance is generated for the project.

The TDL is a performance goal set between the lowest, technically feasible detection limit for routine analytical methods and available regulatory criteria or guidelines for evaluating dredged material. The TDL is, therefore, equal to or greater than the lowest amount of a chemical that can be reliably detected based on the variability of the blank response of routine analytical methods (see EPA [1995] for discussion of method blank response). However, the reliability of a chemical measurement generally increases as the concentration increases. Analytical costs may also be lower at higher detection limits. For these reasons, the TDLs in EPA (1995) have been set at not less than 10 times lower than available regional or international dredged material guidelines for potential biological effects associated with sediment chemical contamination.

All data generated for dredged material evaluation should meet the TDLs in EPA (1995) unless prevented by sample-specific interferences. Any sample-specific interferences must be well documented by the laboratory. If significantly higher or lower TDLs are required to meet rigorously defined data quality

objectives (e.g., for human health risk assessments) for a specific project then, on a project-specific basis, modification to existing analytical procedures may be necessary. Such modifications must be documented in the QA project plan. An experienced analytical chemist should be consulted so the most appropriate method modifications can be assessed, the appropriate coordination with the analytical laboratory can be implemented, and the data quality objectives can be met. A more detailed discussion of method modifications is provided in EPA (1995).

9.3 Chemical Analysis of Sediment

9.3.1 Target Analytes

Chemical analysis provides information about the chemicals present in the dredged material that, if biologically available, could cause toxicity and/or be bioaccumulated. This information is valuable for exposure assessment and for deciding which of the contaminants present in the dredged material to measure in tissue samples.

If the historical review conducted in Tier I (Section 4.1) establishes a reason to believe that sediment contaminants may be present, but fails to produce sufficient information to develop a definitive list of potential contaminants, a list of target analytes has to be compiled. Target analytes should be selected from, but not necessarily limited to, the compounds in Table 9-1 and from the historical review information. The target list should include contaminants that historical information or commercial and/or agricultural applications suggest could be present at a specific dredging site — for example, tributyltin near shipyards, berthing areas, and marinas where these compounds have been applied. Analysis of polynuclear aromatic hydrocarbons (PAH) in dredged material should focus on those PAH compounds that are on the priority pollutant list (Clarke and Gibson, 1987).

All PCB analyses should be made using congener-specific methods. The sum of the concentrations of specific congeners is an appropriate measure of total PCBs (NOAA, 1989).

Sediments should be analyzed for total organic carbon (TOC). This is particularly important if there are hydrophobic organics on the contaminant of concern list developed in Tier I. The TOC content of sediment is a measure of the total amount of oxidizable organic material in a sample and also affects contaminant bioaccumulation by, and effects to, organisms (e.g., Di Toro et al., 1991; DeWitt et al., 1992b).

Table 9-1. Potential Contaminants of Concern Listed According to Structural Compound Class.

Structural Compound Class	Contaminant
Phenols	phenol
	2,4-dimethylphenol
	2-methylphenol
	4-methylphenol
Substituted Phenols	2,4,6-trichlorophenol
	para-chloro-meta-cresol
	2-chlorophenol
	2,4-dichlorophenol
	2-nitrophenol
	4-nitrophenol
	2,4-dinitrophenol
	4,6-dinitro-*o*-cresol
	pentachlorophenol
Organonitrogen Compounds	benzidine
	3,3'-dichlorobenzidine
	2,4-dinitrotoluene
	2,6-dinitrotoluene
	1,2-diphenylhydrazine
	nitrobenzene
	N-nitrosodimethylamine
	N-nitrosodiphenylamine
	N-nitrosodipropylamine
Low Molecular Weight Polynuclear Aromatic Hydrocarbons (PAH)	acenaphthene
	naphthalene
	acenaphthylene
	anthracene
	phenanthrene
	fluorene
	1-methylnapthalene
	2-methylnapthalene
High Molecular Weight Polynuclear Aromatic Hydrocarbons (PAH)	fluoranthene
	benzo*(a)*anthracene
	benzo*(a)*pyrene
	benzo*(b)*fluoranthene
	benzo*(k)*fluoranthene
	chrysene
	benzo*(ghi)*perylene
	dibenzo*(a,h)*anthracene
	ideno(1,2,3-*cd*)pyrene
	pyrene
Chlorinated Aromatic Hydrocarbons	1,2,4-trichlorobenzene
	hexachlorobenzene
	2-chloronaphthalene
	1,2-dichlorobenzene
	1,3-dichlorobenzene
	1,4-dichlorobenzene
Chlorinate Aliphatic Hydrocarbons	hexachlorobutadiene
	hexachloroethane
	hexachlorocyclopentadiene
Halogenated Ethers	bis(2-chloroethyl)ether
	4-chlorophenyl ether
	4-bromophenyl ether
	bis(2-chloroisopropyl) ether
	bis(2-chlorethoxy)methane
Phthalates	bis(2-ethylhexyl)phthalate
	butyl benzyl phthalate
	di-*n*-butyl phthalate
	di-*n*-octyl phthalate
	diethyl phthalate
	dimethyl phthalate
Polychlorinated Biphenyls (PCB) as Aroclors[a]	PCB-1242
	PCB-1254
	PCB-1221
	PCB-1232
	PCB-1248
	PCB-1260
	PCB-1016
Miscellaneous Oxygenated Compounds	TCDD (dioxin)[b]
	PCDF (furan)
	isophorone
Pesticides	aldrin
	dieldrin
	chlordane
	chlorbenside
	dacthal
	DDT[c]
	endosulfan[d]
	endrin
	endrin aldehyde
	heptachlor
	heptachlor epoxide
	α-hexachlorocyclohexane
	β-hexachlorocyclohexane
	δ-hexachlorocyclohexane
	γ-hexachlorocyclohexane
	toxaphene
	mirex
	methoxychlor
	parathion
	malathion
	guthion
	demeton

Table 9-1. *(continued)*

Structural Compound Class	Contaminant
Volatile Halogenated Alkanes	tetrachloromethane
	1,2-dichloroethane
	1,1,1-trichloroethane
	1,1-dichloroethane
	1,1,2-trichloroethane
	1,1,2,2-tetrachloroethane
	chloroethane
	chloroform
	1,2-dichloropropane
	dichloromethane
	chloromethane
	bromomethane
	bromoform
	dichlorobromoethane
	fluorotrichloromethane
	dichlorodifluoromethane
	chlorodibromomethane
Volatile Halogenated Alkenes	1,1-dichlorethylene
	1,2-*trans*-dichlorethylene
	trans-1,3-dichloropropene
	cis-1,3-dichloropropene
	tetrachlorethene
	trichlorethene
	vinyl chloride
Volatile Aromatic Hydrocarbons	benzene
	ethylbenzene
	toluene
Chlorinated Benzenes	1,3-dichlorobenzene
	1,4-dichlorobenzene
	1,2-dichlorobenzene
	1,2,4-trichlorobenzene
	hexachlorobenzene
Volatile Unsaturated Carbonyl Compounds	acrolein
	acrylonitrile
Volatile Ethers	2-chlorethylvinylether
	bis(chloromethyl)ether
Metals	aluminum
	antimony
	arsenic
	beryllium
	butyltins
	cadmium
	chromium (hexavalent)
	cobalt
	copper
	iron
	lead
	manganese
	mercury
	nickel
	selenium
	silver
	thallium
	tin
	zinc
Miscellaneous	ammonia[e]
	asbestos
	benzoic acid
	cyanide
	guaiacols
	methylethyl ketone
	resin acids

[a]It is recommended that PCB analyses use congener-specific methods. The sum of the concentrations of specific congeners is an appropriate measure of total PCBs (see Table 9-3).
[b]Additional dioxin and furan (e.g., TCDF) compounds are listed in Table 9-2.
[c]Includes DDT, DDD, and DDE
[d]Includes ∝-endosulfan, β-endosulfan, and endosulfan sulfate.
[e]Ammonia may not be a contaminant of concern at certain open-water dredged material disposal sites (e.g., dispersive situations and situations with well-oxygenated overlying water).

Sediments in which metals are suspected to be contaminants of concern may also be analyzed for acid volatile sulfide (AVS) (Di Toro et al., 1990; EPA, 1991a). Although acceptable guidance on the interpretation of AVS measurements is not yet available, and AVS measurements are not generally recommended at this time, such measurements can provide information on the bioavailability of metals in anoxic sediments. Presently, AVS studies represent an area of on-going research which may be formally included in the manual if and when decision criteria are determined.

9.3.2 Selection of Analytical Techniques

Once the list of target analytes for sediments has been established, analytical methods have to be determined. The methods will, to some degree, dictate the amount of sediment sample required for each analysis. General sample sizes are provided in Table 8-2, and include possible requirements for more than one analysis for each group of analytes. The amount of sample used in an analysis affects the detection limits attainable by a particular method.

TOC analyses should be based on high-temperature combustion rather than on chemical oxidation. Some classes of organic compounds are not fully degraded by chemical/ultraviolet techniques. The volatile and nonvolatile organic components make up the TOC of a sample. Because inorganic carbon (e.g., carbonates and bicarbonates) can be a significant proportion of the total carbon in some sediment, the sample has to be treated with acid to remove the inorganic carbon prior to TOC analysis. The method of Plumb (1981) recommends HCl as the acid. An alternative choice might be sulfuric acid since it is nonvolatile, is used as the preservative, and does not add to the chloride burden of the sample. Whatever acid is used, it has to be demonstrated on sodium chloride blanks that there is no interference generated from the combined action of acid and salt in the sample. Acceptable methods for TOC analysis are available from EPA (1995).

For many metals analyses in marine/estuarine areas, the concentration of salt may be much greater than the analyte of interest and can cause unacceptable interferences in certain analytical techniques. In such cases, the freshwater approach of acid digestion followed by inductively coupled plasma-atomic emission spectrometry (ICP) or graphite furnace atomic absorption spectroscopy (GFAAS) should be coupled with appropriate techniques for controlling this interference. The Hg method in EPA (1986a; Method 7471) may be used for the analysis of Hg in sediment. Tributyltin may be analyzed by the method of Rice et al. (1987), and selenium and arsenic by the method of EPRI (1986). A total extraction of metal ions is neither necessary nor desirable for dredged material evaluations. The standard aqua regia extraction yields consistent and reproducible results.

The recommended method for analysis of semivolatile and volatile priority pollutants in sediment is described by Tetra Tech (1986a). Analysis for organic compounds should always use capillary-column gas chromatography (GC): gas chromatography/mass spectrometry (GC/MS) techniques for semi-volatile and volatile priority pollutants, and dual column gas chromatography/electron-capture detection (GC/ECD) for pesticides and PCBs (NOAA, 1989). Alternatively, GC/MS using selected ion monitoring can be used for PCB and pesticide analysis. These analytically sound techniques yield accurate data on the concentrations of chemicals in the sediment matrix. The analytical techniques for semivolatile organic compounds generally involve solvent extraction from the sediment matrix and subsequent analysis, after cleanup, using GC or GC/MS. Extensive cleanup is necessitated by the likelihood of (1) biological macromolecules, (2) sulfur from sediments with low or no oxygen, and (3) oil and/or grease in the sediment. The analysis of volatile organic compounds incorporates purge-and-trap techniques with analysis by either GC or GC/MS. If dioxin (i.e., 2,3,7,8, - TCDD) analysis is being performed, the methods of Kuehl et al. (1987), Smith et al. (1984), EPA (1989b; Method 8290), or EPA (1990c; Method 1613) and summary in EPA (1995) should be consulted. EPA Method 1613 is the recommended procedure for measuring the tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). This method has been developed for analysis of water, soil, sediment, sludge, and tissue. Table 9-2 shows the 17 compounds determined by Method 1613.

Techniques for analysis of chemical constituents have some inherent limitations for sediment samples. Interferences encountered as part of the sediment matrix, particularly in samples from heavily contaminated areas, may limit the ability of a method to detect or quantify some analytes. The most selective methods using GC/MS techniques are recommended for all nonchlorinated organic compounds because such analysis can often avoid problems due to matrix interferences. Gas chromatography/electron-capture detection (GC/ECD) methods are recommended as the primary analytical tool for all PCB and pesticide analyses because GC/ECD analysis will result in lower detection limits. The analysis and identification of PCBs by GC/ECD methods are based upon relative retention times and peak shapes. Matrix interferences may result in the reporting of false negatives, although congener-specific PCB analysis reduces this concern relative to use of the historical Aroclor® matching procedure.

PCBs have traditionally been quantified with respect to Aroclor® mixtures. This procedure can result in errors in determining concentrations (Brown et al., 1984). For dredged material evaluations, the concentration of total PCBs should be determined by summing the concentrations of specific individual PCB congeners identified in the sample (see Table 9-3). The minimum number of PCB congeners that should be analyzed are listed in the first column of Table 9-3 (i.e., "summation" column) (NOAA, 1989). This summation is considered the most accurate representation of the PCB concentration in samples. Additional PCB congeners are also listed in Table 9-3. McFarland and Clarke (1989) recommend these PCB congeners for analysis based on environmental abundance, persistence, and biological importance.

Table 9-2. PCDD and PCDF Compounds Determined by Method 1613

Native Compound[1]
2,3,7,8-TCDF
2,3,7,8-TCDD
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD
1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDF
1,2,3,4,6,7,8-HpCDD
1,2,3,4,7,8,9-HpCDF
OCDD
OCDF

[1] Polychlorinated dioxins and furans:

TCDD = Tetrachlorodibenzo-p-dioxin
TCDF = Tetrachlorodibenzofuran
PeCDD = Pentachlorodibenzo-p-dioxin
PeCDF = Pentachlorodibenzofuran
HxCDD = Hexachlorodibenzo-p-dioxin
HxCDF = Hexachlorodibenzofuran
HpCDD = Heptachlorodibenzo-p-dioxin
HpCDF = Heptachlorodibenzofuran
OCDD = Octachlorodibenzo-p-dioxin
OCDF = Octachlorodibenzofuran

Table 9-3. Polychlorinated Biphenyl (PCB) Congeners Recommended for Quantitation as Potential Contaminants of Concern.

PCB Congener[a]	Congener Number[b]		
	Summation[c]	Highest Priority[d]	Second Priority[e]
2,4' diCB	8		
2,2',5 triCB	18		18
2,4,4' triCB	28		
3,4,4' triCB			37
2,2',3,5' tetraCB	44		44
2,2',4,5' tetraCB			99
2,2',5,5' tetraCB	52		52
2,3',4,4' tetraCB	66		
2,3',4',5 tetraCB			70
2,4,4',5 tetraCB			74
3,3',4,4' tetraCB	77	77	
3,4,4',5 tetraCB			81
2,2',3,4,5' pentaCB		87	
2,2',3,4',5 pentaCB		49	
2,2',4,5,5' pentaCB	101	101	
2,3,3',4,4' pentaCB	105	105	
2,3,4,4',5 pentaCB			114
2,3',4,4',5 pentaCB	118	118	
2,3',4,4',6 pentaCB			119
2',3,4,4',5 pentaCB			123
3,3',4,4',5 pentaCB	126[f]	126[f]	
2',3,3',4,4' hexaCB	128	128	
2,2',3,4,4',5' hexaCB	138	138	
2,2',3,5,5',6 hexaCB			151
2,2',4,4',5,5' hexaCB	153	153	
2,3,3',4,4',5 hexaCB		156	
2,3,3',4,4',5 hexaCB			157
2,3,3',4,4',6 hexaCB			158
2,3',4,4',5,5' hexaCB			167
2,3',4,4',5',6 hexaCB			168
3,3',4,4',5,5' hexaCB	169[f]	169[f]	
2,2',3,3',4,4',5 heptaCB	170	170	
2,2',3,4,4',5,5' heptaCB	180	180	
2,2',3,4,4',5',6 heptaCB		183	
2,2',3,4,4',6,6' heptaCB		184	
2,2',3,4',5,5',6 heptaCB	187		187
2,3,3',4,4',5,5' heptaCB			189

(continued)

Table 9-3. *(continued)*

PCB Congener[a]	Congener Number[b]		
	Summation[c]	Highest Priority[d]	Second Priority[e]
2,2',3,3',4,4',5,6 octaCB		195	
2,2',3,3',4,5,5',6' octaCB			201
2,2',3,3',4,4',5,5',6 nonaCB		206	
2,2',3,3',4,4',5,5',6,6' decaCB		209	

[a]PCB congeners recommended for quantitation, from dichlorobiphenyl (diCB) through decachlorobiphenyl (decaCB).

[b]Congeners are identified by their International Union of Pure and Applied Chemistry (IUPAC) number, as referenced in Ballschmiter and Zell (1980) and Mullin et al. (1984).

[c]These congeners are summed to determine total PCB concentration following the approach in NOAA (1989).

[d]PCB congeners having highest priority for potential environmental importance based on potential for toxicity, frequency of occurrence in environmental samples, and relative abundance in animal tissues (McFarland and Clarke, 1989).

[e]PCB congeners having second priority for potential environmental importance based on potential for toxicity, frequency of occurrence in environmental samples, and relative abundance in animal tissues (McFarland and Clarke, 1989).

[f]To separate PCBs 126 and 169, it is necessary to initially utilize an enrichment step with an activated carbon column (Smith, 1981).

McFarland et al. (1986) note that the most toxic PCB congeners lie mainly within the tetra-, penta-, and hexa- chlorobiphenyl groups. Sample preparation for PCB congener analysis should follow the techniques described by Tetra Tech (1986a) or EPA (1986a), but with instrumental analysis and quantification using standard capillary GC columns on individual PCB isomers according to the methods reported by NOAA (1989) (see also Dunn et al., 1984; Schwartz et al., 1984; Mullin et al., 1984; Stalling et al., 1987).

Although the methods mentioned above are adequate for detecting and quantifying concentrations of those PCB congeners comprising the majority of total PCBs in environmental samples, they are not appropriate for separating and quantifying PCB congeners which may coelute with other congeners and/or may be present at relatively small concentrations in the total PCB mixture. Included in this latter group of compounds, for example, are PCBs 126 and 169, two of the more toxic nonortho-substituted (coplanar) PCB congeners (Table 9-3). In order to separate these (and other toxic nonortho-substituted congeners), it is necessary to initially utilize an enrichment step with an activated carbon column (Smith, 1981). Various types of carbon columns have been used, ranging from simple gravity columns (e.g., in a Pasteur pipette) to more elaborate (and efficient) columns using high pressure liquid chromatography (HPLC) systems (see Schwartz et al., 1993). The preferred method of separation and quantitation of the enriched PCB mixture has been via high resolution GC-MS with isotope dilution (Kuehl et al., 1991; Ankley et al., 1993; Schwartz et al., 1993). However, recent studies have shown that if the carbon enrichment is done via HPLC, the nonortho-substituted PCB congeners of concern also may be quantifiable via more widely available GC/ECD systems (Schwartz et al., 1993).

The overall toxicity of nonortho-substituted PCBs at a site can be assessed based on a comparison with the toxicity of 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD). A similar procedure can be used for assessing the toxicity of a mixture of dioxins and furans. In this "toxicity equivalency factor" (TEF) approach, potency values of individual congeners (relative to TCDD) and their respective sediment concentrations are used to derive a "summed" 2,3,7,8-TCDD equivalent (TCDD-EQ) (EPA, 1989c; Table 9-4). Ankley et al. (1992b) provide an example of the use of this approach.

TEFs have been derived for human health purposes. For aquatic organisms the relative toxicities of different PCB congeners and dioxins are likely to be quite different. For instance, wildlife or fish TEF for PCBs are not equivalent to those for humans (Walker et al., 1992).

To ensure that contaminants not included in the list of target analytes are not overlooked in the chemical characterization of the dredged material, the analytical results should also be scrutinized by trained personnel. The presence of persistent major unknown analytes should be noted. Methods involving GC/MS techniques for organic compounds are recommended for the identification of any unknown analytes.

Table 9-4. Methodology for Toxicity Equivalency Factors

Because toxicity information on some dioxin and furan species is scarce, a structure-activity relationship has been assumed. The toxicity of each congener is expressed as a fraction of the toxicity of 2,3,7,8 TCDD.

Compound	TEF
2,3,7,8 TCDD	1
other TCDD	0
2,3,7,8-PeCDDs	0.5
other PeCDDs	0
2,3,7,8-HxCDDs	0.1
other HxCDDs	0
2,3,7,8-HpCDDs	0.01
other HpCDDs	0
OCDD	0.001
2,3,7,8-TCDF	0.1
other TCDFs	0
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
other PeCDFs	0
2,3,7,8-HxCDFs	0.1
other HxCDFs	0
2,3,7,8-HpCDFs	0.01
other HpCDFs	0
OCDF	0.001

9.4 Chemical Analysis of Water

9.4.1 Analytical Targets

Analysis to determine the potential release of dissolved contaminants from the dredged material (standard elutriate) may be necessary to make a factual determination. Elutriate tests (Section 10.1.2.1) involve mixing dredged material with dredging site water and allowing the mixture to settle. The portion of the dredged material that is considered to have the potential to impact the water column is the supernatant remaining after undisturbed settling and centrifugation. Chemical analysis of the elutriate allows a direct comparison, after allowance for mixing, to applicable water quality standards (WQS). When collecting samples for elutriate testing, consideration should be given to adequate volumes of water and sediment required to prepare samples for analysis including replicates where appropriate. In some instances, when there is poor settling, the elutriate preparation has to be performed successively several times to accumulate enough water for testing.

Historical water quality information from the dredging site (Tier I) should be evaluated along with data obtained from the chemical analysis of sediment samples to select target analytes. Chemical evaluation of the dredged material provides a known list of constituents which might affect the water column. All target analytes identified in the sediment should initially be considered potential targets for water analysis. Nonpriority-pollutant chemical components which are found in measurable concentrations in the sediments should be included as targets if review of the literature indicates that these analytes have the potential to bioaccumulate in animals [i.e., have a high K_{ow} or bioconcentration factor (BCF)] and/or are of toxicological concern.

9.4.2 Analytical Techniques

In contrast to freshwater, there generally are no EPA approved methods for analysis of saline water although widely accepted methods have existed for some time (e.g., Strickland and Parsons, 1972; Grasshoff et al., 1983; Parsons et al., 1984). Application of the freshwater methods to saltwater will frequently result in higher detection limits than are common for freshwater unless care is taken to control the effects of salt on the analytical signal. Modifications or substitute methods (e.g., additional extract concentration steps, larger sample sizes, or concentration of extracts to smaller volumes) might be necessary to properly determine analyte concentration in seawater or to meet the desired target detection limits (TDLs). It is extremely important to ascertain a laboratory's ability to execute methods and attain acceptable detection limits in matrices containing up to 3% sodium chloride.

Once the list of target analytes for water has been established, analytical methods have to be determined. The water volume required for specific analytical methods may vary. A minimum of 1 L of elutriate should be prepared for metals analysis (as little as 100 mL may be analyzed). One liter of elutriate should be analyzed for organic compounds. Sample size should also include the additional volume required for the matrix spike and matrix spike duplicate analyses required as part of the analytical procedure. Samples from the dredging site and, where appropriate, disposal site, should be delivered for organic and metals analysis. Sample size is one of the limiting factors in determining detection limits for water analyses, but TDLs below the WQS must be the goal in all cases. Participating laboratories should routinely report detection limits achieved for a given analyte.

Detailed methods for the analysis of organic and inorganic priority pollutants in water are referenced in 40 CFR 136 and in EPA (1983). Additional approved methods include EPA (1986a,b; 1988a,b,c; 1990b,c); APHA (1989); ASTM (1991b); Tetra Tech (1985). Most of these methods will require modification to achieve low detection limits in saline waters. Analysis of the semivolatile organic priority pollutants involves a solvent extraction of water with an optional sample cleanup procedure and analysis using GC or GC/MS. The volatile priority pollutants are determined by using purge-and-trap techniques and are analyzed by either GC or GC/MS. If dioxin (i.e., 2,3,7,8, - TCDD) analysis is necessary, Kuehl et al. (1987), Smith et al. (1984), EPA (1989b; Method 8290), or EPA (1990c; Method 1613) should be consulted. EPA Method 1613 is the recommended procedure for measuring the tetra- through octa-PCDDs and PCDFs.

A primary requirement for analysis of inorganic and organic priority pollutants is to obtain detection limits which will result in usable, quantitative data that can subsequently be compared against applicable WQS to determine compliance with the water quality certification requirement under Section 401. Existing EPA methods for freshwater analysis need to be adapted to achieve environmentally meaningful detection limits in saline waters because of matrix interferences caused by salt. For example, it is recommended that sample extracts be concentrated to the lowest possible volume prior to instrumental analysis, and that instrumental injection volumes be increased to lower the detection limits. All PCB and pesticide analytes should be analyzed by using GC/ECD, since the GC/ECD methods are more sensitive to these compounds and will lower the detection limits. PCBs should be quantified as specific congeners (Mullin et al., 1984; Stalling et al., 1987) and as total PCBs based on the summation of particular congeners (NOAA, 1989).

Analysis of saline water for metals is subject to matrix interferences from salts, particularly sodium and chloride ions, when the samples are concentrated prior to instrumental analysis. The gold-amalgamation method using cold-vapor atomic absorption spectrophotometry (AAS) analysis is recommended to eliminate saline water matrix interferences for mercury analysis. Methods using solvent extraction and

AAS analysis may be required to reduce saline water matrix interferences for other target metals. Other methods appropriate for metals include: cadmium, copper, lead, iron, zinc, silver (Danielson et al., 1978); arsenic (EPRI, 1986); selenium and antimony (Sturgeon et al., 1985); low levels of mercury (Bloom et al., 1983); and, tributyltin (Rice et al., 1987). Graphite-furnace AAS techniques after extraction are recommended for the analysis of metals, with the exception of mercury.

9.5 Chemical Analysis of Tissues

9.5.1 Target Analytes

Bioaccumulation is evaluated by analyzing tissues of test organisms for contaminants determined to be of concern for a specific dredged material. Sediment contaminant data and available information on the bioaccumulation potential of those analytes have to be interpreted to establish target compounds.

The *n*-octanol/water partition coefficient (K_{ow}) is used to estimate the BCFs of chemicals in organism/water systems (Chiou et al., 1977; Kenaga and Goring, 1980; Veith et al., 1980; Mackay, 1982). The potential for bioaccumulation generally increases as K_{ow} increases, particularly for compounds with log K_{ow} less than approximately 6. Above this value, there is less of a tendency for bioaccumulation potential to increase with increasing K_{ow}. Consequently, the relative potential for bioaccumulation of organic compounds can be estimated from the K_{ow} of the compounds. EPA (1985) recommends that compounds for which the log K_{ow} is greater than 3.5 be considered for further evaluation of bioaccumulation potential. The organic compound classes of priority pollutants with the greatest potential to bioaccumulate are PAHs, PCBs, pesticides, and some phthalate esters. Generally, the volatile organic, phenol, and organonitrogen priority pollutants are not readily bioaccumulated, but exceptions include the chlorinated benzenes and the chlorinated phenols. Table 9-5 provides data for organic priority pollutants based on K_{ow}. Specific target analytes for PCBs and PAHs are discussed in Section 9.3.1. The water content and percent lipids should be routinely determined as part of tissue analyses for organic contaminants.

Table 9-6 ranks the bioaccumulation potential of the inorganic priority pollutants based on calculated BCFs. Dredged material contaminants with BCFs greater than 1,000 (log BCF >3) should be further evaluated for bioaccumulation potential.

Tables 9-5 and 9-6 should be used with caution because they are based on calculated bioconcentration from water. Sediment bioaccumulation tests, in contrast, are concerned with accumulation from a complex medium via all possible routes of uptake. The appropriate use of the tables is to help in selecting

Table 9-5. Octanol/Water Partition Coefficients (K_{ow}) for Organic Compound Priority Pollutants and 301(h) Pesticides[a].

Pollutant	Octanol/Water Partition Coefficient (log K_{ow})	Pollutant	Octanol/Water Partition Coefficient (log K_{ow})
Di-*n*-octyl phthalate	9.2	Acenaphthylene	4.1
Indeno(1,2,3-*cd*)pyrene	7.7	Butyl benzyl phthalate	4.0
Benzo(*ghi*)perylene	7.0	PCB-1221	4.0
PCB-1260	6.9	Hexachloroethane	3.9
Mirex[b]	6.9	Acenaphthene	3.9
Benzo(*k*)fluoranthene	6.8	α-hexachlorocyclohexane	3.8
Benzo(*b*)fluoranthene	6.6	δ-hexachlorocyclohexane	3.8
PCB-1248	6.1	ß-hexachlorocyclohexane	3.8
2,3,7,8-TCDD (dioxin)	6.1	γ-hexachlorocyclohexane	3.8
Benzo(*a*)pyrene	6.0	Parathion[b]	3.8
Chlordane	6.0	Chlorobenzene	3.8
PCB-1242	6.0	2,4,6-trichlorophenol	3.7
4,4'-DDD	6.0	ß-endosulfan	3.6
Dibenzo(*a,h*)anthracene	6.0	Endosulfan sulfate	3.6
PCB-1016	5.9	α-endosulfan	3.6
4,4'-DDT	5.7	Naphthalene	3.6
4,4'-DDE	5.7	Fluorotrichloromethane[c]	3.5
Benzo(*a*)anthracene	5.6	1,4-dichlorobenzene	3.5
Chrysene	5.6	1,3-dichlorobenzene	3.4
Endrin aldehyde	5.6	1,2-dichlorobenzene	3.4
Fluoranthene	5.5	Toxaphene	3.3
Hexachlorocyclopentadiene	5.5	Ethylbenzene	3.1
Dieldrin	5.5	*N*-nitrosodiphenylamine	3.1
Heptachlor	5.4	*P*-chloro-*m* cresol	3.1
Heptachlor epoxide	5.4	2,4-dichlorophenol	3.1
Hexachlorobenzene	5.2	3,3'-dichlorobenzene	3.0
Di-*n*-butyl phthalate	5.1	Aldrin	3.0
4-Bromophenyl phenyl ether	5.1	1,2-diphenylhydrazine	2.9
Pentachlorophenol	5.0	4-nitrophenol	2.9
4-Chlorophenyl phenyl ether	4.9	Malathion[b]	2.9
Pyrene	4.9	Tetrachloroethene	2.9
2-Chloronaphthalene	4.7	4,6-dinitro-*o*-cresol	2.8
Endrin	4.6	Tetrachloroethene	2.6
PCB-1232	4.5	Bis(2-chloroisopropyl)ether	2.6
Phenanthrene	4.5	1,1,1-trichloroethane	2.5
Fluorene	4.4	Trichloroethene	2.4
Anthracene	4.3	2,4-dimethylphenol	2.4
Methoxychlor[b]	4.3	1,1,2,2-tetrachloroethane	2.4
Hexachlorobutadiene	4.3	Bromoform	2.3
1,2,4-trichlorobenzene	4.2	1,2-dichloropropane	2.3
Bis(2-ethylhexyl)phthalate	4.2	Toluene	2.2

Table 9-5. *(continued)*

Pollutant	Octanol/Water Partition Coefficient (log K_{ow})	Pollutant	Octanol/Water Partition Coefficient (log K_{ow})
1,1,2-trichloroethane	2.2	Dimethyl phthalate	1.6
Guthion[b]	2.2	Chloroethane	1.5
Dichlorodiflouromethane[c]	2.2	2,4-dinitrophenol	1.5
2-chlorophenol	2.2	1,1-dichloroethylene	1.5
Benzene	2.1	Phenol	1.5
Chlorodibromomethane	2.1	1,2-dichloroethane	1.4
2,4-dinitrotoluene	2.1	Diethyl phthalate	1.4
2,6-dinitrotoluene	2.0	*N*-nitrosodipropylamine	1.3
Trans-1,2-dichloropropene	2.0	Dichloromethane	1.3
Cis-1,3-dichloropropene	2.0	2-chloroethylvinylether	1.3
Demeton[b]	1.9	Bis(2-chloroethoxy)methane	1.3
Chloroform	1.9	Acrylonitrile	1.2
Dichlorobromomethane	1.9	Bis(2-chloroethyl)ether	1.1
Nitrobenzene	1.9	Bromomethane	1.0
Benzidine	1.8	Acrolein	0.9
1,1-dichloroethane	1.8	Chloromethane	0.9
2-nitrophenol	1.8	Vinyl chloride	0.6
Isophorone	1.7	*N*-nitrosodimethylamine	0.6

[a]Adapted from Tetra Tech (1985).
[b]301(h) pesticides not on the priority pollutant list.
[c]No longer on priority pollutant or 301(h) list.

[Note: Mixtures, such as PCB Aroclors®, cannot have discrete K_{ow} values, however, the value given is a rough estimate for the mean. It is recommended that all PCB analyses use congener-specific methods. All PCB congeners have a log K_{ow} >4 (L. Burkhardt, EPA Duluth, pers. comm.).]

Table 9-6. Bioconcentration Factors (BCF) of Inorganic Priority Pollutants.[a]

Inorganic Pollutant	Log BCF[b]
Metals	
Methylmercury	4.6
Phenylmercury	4.6
Mercuric acetate	3.5
Copper	3.1
Zinc	2.8
Arsenic	2.5
Cadmium	2.5
Lead	2.2
Chromium IV	2.1
Chromium III	2.1
Mercury	2.0
Nickel	1.7
Thallium	1.2
Antimony	ND
Silver	ND
Selenium	ND
Beryllium	ND
Nonmetals	
Cyanide	ND
Asbestos	ND

[a]Adapted from Tetra Tech (1986b).
[b]ND: No data.

contaminants of concern for bioaccumulation analysis by providing a general indication of the relative potential for various chemicals to accumulate in tissues.

The strategy for selecting contaminants for tissue analysis should include three considerations, all of which are related to regulatory concern:

- the target analyte is a contaminant of concern and is present in the sediment as determined by sediment chemical analyses
- the target analyte has a high potential to accumulate and persist in tissues
- the target analyte is of toxicological concern.

Contaminants with a lower potential to bioaccumulate, but which are present at high concentrations in the sediments, should also be included in the target list because bioavailability can increase with concentration. Conversely, contaminants with a high accumulation potential and of high toxicological concern should be considered as targets, even if they are only present at low concentrations in the sediment. Nonpriority-pollutant contaminants which are found in measurable concentrations in the sediments should be included as targets for tissue analysis if they have the potential to bioaccumulate and persist in tissues, and are of toxicological concern.

9.5.2 Analytical Techniques

At present, formally approved standard methods for the analysis of priority pollutants and other contaminants in tissues are not available. However, studies conducted for EPA and other agencies have developed analytical methods capable of identifying and quantifying most organic and inorganic priority pollutants in tissues. The amount of tissue required for analysis is dependent on the analytical procedure and the tissue moisture content. General guidance, but *not* firm recommendations, for the amount of tissue required, is provided in Table 8-2. The required amounts may vary depending on the analytes, matrices, detection limits, and particular analytical laboratory. Tissue moisture content must be determined for each sample to convert applicable data from a wet-weight to a dry-weight basis, however both wet- and dry-weight data should be reported.

Detection limits depend on the sample size as well as the specific analytical procedure. TDLs should be determined for all analytes according to initial guidance in 40 CFR 136 and more definitive guidance in

EPA (1995; cf. Section 9.2). Detection limits should be specified based on the intended use of the data and specific needs of each evaluation.

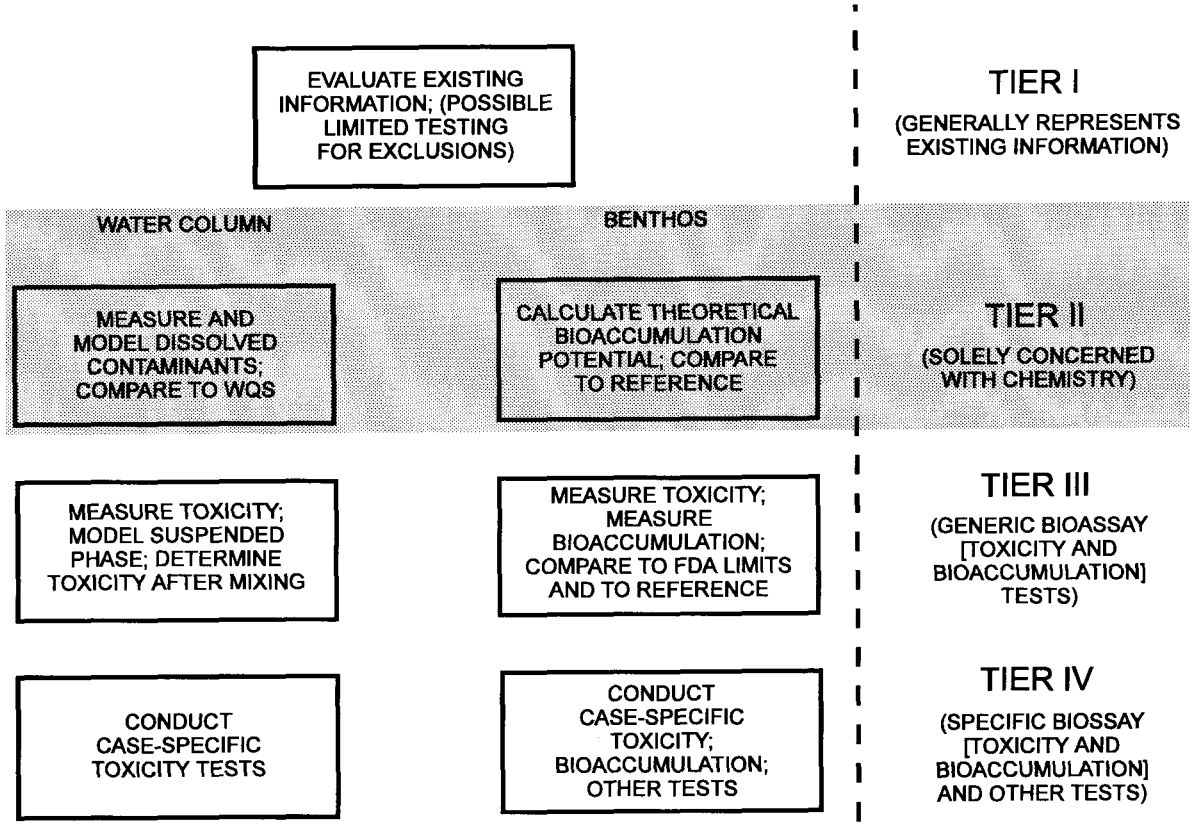
Existing methods for priority pollutant tissue analysis involve two separate procedures: one for organic compounds and another for metals. The recommended methods for the analysis of semivolatile organic pollutants are described in NOAA (1989). The procedure involves serial extraction of homogenized tissue samples with methylene chloride, followed by alumina and gel-permeation column cleanup procedures that remove coextracted lipids. An automated gel-permeation procedure described by Sloan et al. (1993) is recommended for rapid, efficient, reproducible sample cleanup. The extract is concentrated and analyzed for semivolatile organic pollutants using GC with capillary fused-silica columns to achieve sufficient analyte resolution. If dioxin (i.e., 2,3,7,8-TCDD) analysis is being performed, the methods of Mehrle et al. (1988), Kuehl et al. (1987), Smith et al. (1984), EPA (1989b; Method 8290), or EPA (1990c; Method 1613) should be consulted. EPA Method 1613 is the recommended procedure for measuring the tetra- through octa-PCDDs and PCDFs.

Chlorinated hydrocarbons (e.g., PCBs and chlorinated pesticides) should be analyzed by GC/ECD. PCBs should be quantitated as specific congeners (Mullin et al., 1984; Stalling et al., 1987) and not by industrial formulations (e.g., aroclors) because the levels of PCBs in tissues result from complex processes, including selective accumulation and metabolism (see the discussion of PCBs in Section 9.3.2). Lower detection limits and positive identification of PCBs and pesticides can be obtained by using chemical ionization mass spectrometry.

The same tissue extract is analyzed for other semivolatile pollutants (e.g., PAHs, phthalate esters, nitrosamines, phenols, etc.) using GC/MS as described by NOAA (1989), Battelle (1985), and Tetra Tech (1986b). These GC/MS methods are similar to EPA Method 8270 for solid wastes and soils (EPA, 1986a). Lowest detection limits are achieved by operating the mass spectrometer in the SIM mode. Decisions to perform analysis of nonchlorinated hydrocarbons and resulting data interpretation should consider that many of these analytes are readily metabolized by most fish and many invertebrates. Analytical methods for analysis of tissue samples for volatile priority pollutants are found in Tetra Tech (1986b).

Tissue lipid content is of importance in the interpretation of bioaccumulation information. A lipid determination should be performed on biota submitted for organic analysis if: (1) food chain models will be used; (2) test organisms could spawn during the test; (3) special circumstances occur (Tier IV), such as those requiring risk assessment. Bligh and Dyer (1959) provide an acceptable method, and the various available methods are evaluated by Randall et al. (1991).

Analysis for priority pollutant metals involves a nitric acid or nitric acid/perchloric acid digestion of the tissue sample and subsequent analysis of the acid extract using AAS or inductively coupled plasma-atomic emission spectrometry (ICP) techniques. Procedures in Tetra Tech (1986b) and EPA (1991c) are generally recommended. NOAA (1989) methods may also be used and are recommended when low detection levels are required. Microwave technology may be used for tissue digestion to reduce contamination and to improve recovery of metals (Nakashima et al., 1988). This methodology is consistent with tissue analyses performed by NOAA (1989), except for the microwave heating steps. Mercury analysis requires the use of cold-vapor AAS methods (EPA, 1991c). The matrix interferences encountered in analysis of metals in tissue may require case-specific techniques for overcoming interference problems. If tributyltin analysis is being performed, the methods of Rice et al. (1987) or Uhler et al. (1989) should be consulted.


EVALUATE EXISTING INFORMATION; (POSSIBLE LIMITED TESTING FOR EXCLUSIONS)
TIER I
(GENERALLY REPRESENTS EXISTING INFORMATION)
WATER COLUMN
BENTHOS
MEASURE AND MODEL DISSOLVED CONTAMINANTS; COMPARE TO WQS
CALCULATE THEORETICAL BIOACCUMULATION POTENTIAL; COMPARE TO REFERENCE
TIER II
(SOLELY CONCERNED WITH CHEMISTRY)
MEASURE TOXICITY; MODEL SUSPENDED PHASE; DETERMINE TOXICITY AFTER MIXING
MEASURE TOXICITY; MEASURE BIOACCUMULATION; COMPARE TO FDA LIMITS AND TO REFERENCE
TIER III
(GENERIC BIOASSAY [TOXICITY AND BIOACCUMULATION] TESTS)
CONDUCT CASE-SPECIFIC TOXICITY TESTS
CONDUCT CASE-SPECIFIC TOXICITY; BIOACCUMULATION; OTHER TESTS
TIER IV
(SPECIFIC BIOSSAY [TOXICITY AND BIOACCUMULATION] AND OTHER TESTS)